sity, 1966 (unpublished).
[6]J. M. Bridges and W. L. Wiese, to be published.
[7]D. E. Roberts, Phys. Letters 22, 417 (1966).
[8]J. R. Roberts and K. L. Eckerle, to be published.
[9]H. R. Griem, Plasma Spectroscopy (McGraw-Hill Book Company, New York, 1964).
[10]H. R. Griem, M. Baranger, A. C. Kolb, and G. K. Oertel, Phys. Rev. 125, 177 (1962); hereafter referred to as GBKO.
[11]G. K. Oertel, Bull. Am. Phys. Soc., to be published.
[12]H. R. Griem, Phys. Rev. Letters 17, 509 (1966).
[13]J. Cooper, Phys. Rev. Letters 17, 991 (1966).
[14]M. Baranger, Phys. Rev. 112, 885 (1958).
[15]M. Baranger, in Atomic and Molecular Processes, edited by D. R. Bates (Academic Press, Inc., New York, 1962), Sec. 44, p. 526.
[16]K. Alder, A. Bohr, T. Huus, B. Mottelson, and A. Winther, Rev. Mod. Phys. 28, 432 (1956).
[17]R. A. Day, private communication.
[18]M. J. Seaton, Proc. Phys. Soc. (London) 79, 1105 (1962).
[19]J. Cooper and G. K. Oertel, to be published.
[20]H. R. Griem, Phys. Rev. 128, 515 (1962).
[21]Charlotte E. Moore, Atomic Energy Levels, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington, D. C., 1958).

VELOCITY AUTOCORRELATIONS FOR HARD SPHERES*

B. J. Alder and T. E. Wainwright
Lawrence Radiation Laboratory, University of California, Livermore, California
(Received 1 May 1967)

A study of the velocity autocorrelation function for hard spheres over the entire fluid density region shows that deviations from exponential behavior are small. At very low density a small positive deviation is found which is accounted for in the Boltzmann theory of the self-diffusion coefficient. At higher densities the principal non-Markovian process is identified with a surprisingly long persistence of velocity currents. At still higher densities, near solidification, anticorrelating backscattering events predominate.

The principal difficulty in calculating transport coefficients concerns the estimation of the contribution of various correlated or non-Markovian events. An effort to evaluate these systematically as a function of increasing density has led in recent years to the unexpected conclusion that the transport coefficients, unlike the thermodynamic properties, cannot be represented by a power series in the density; terms in the logarithm of the density appear as well.[1] Since the magnitude of these logarithmic terms is not yet known from theoretical calculations, their quantitative significance remains in doubt. This Letter describes an attempt to evaluate these terms for a hard-sphere system by a molecular dynamics study[2] in which the structure of the velocity autocorrelation function is examined at a series of densities.

Before studying the density dependence of the transport coefficients, it is necessary to establish that the method to be employed is able to give the correct low-density behavior as predicted by the Boltzmann equation. Doubt about the accuracy of the molecular dynamic method concerns only how well a finite number of particles can represent an infinite system. This doubt has been dispelled in the usual empirical fashion by studying both a 108- and a 500-particle system with the same periodic boundary conditions and finding only a slightly different behavior, that is $D_N \sim D_\infty(1-2/N)$, where N is the number of particles and D_N the corresponding diffusion coefficient.

Calculations of the velocity autocorrelation function at a density so low (100 times the close-packed volume V_0) that the third virial coefficient contributes only about 1 % as much as the second reveals a small positive deviation from exponential behavior (see Fig. 1). The diffusion coefficient obtained after the $1/N$ correction has been made is in good agreement with the one obtained from the Boltzmann equation[3] (see Fig. 2). This agreement represents an independent, numerical verification of the Boltzmann equation.

A purely exponentially decaying autocorrelation function leads to a value of the self-diffusion coefficient equal to the one calculated from the Boltzmann equation to zeroth order in the Sonine polynomial expansion.[4] Since the complete Sonine polynomial solution leads only to a 1.9% increase in the diffusion coefficient, it is clear that at low densities a small positive deviation from exponential behavior is to be expected. The velocity autocorrelation function itself has apparently not yet been theoret-

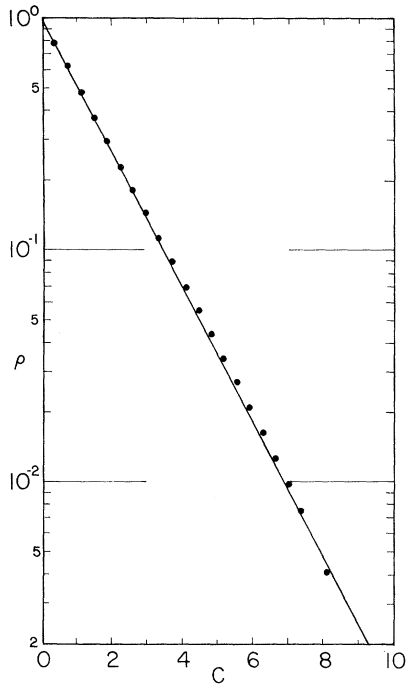

FIG. 1. The velocity autocorrelation function versus the number of mean collision times for 108 particles at $V/V_0 = 100$. The nearly exponential behavior is illustrated by the comparison of the computer data (dots) with the theoretically determined exponential (straight line).

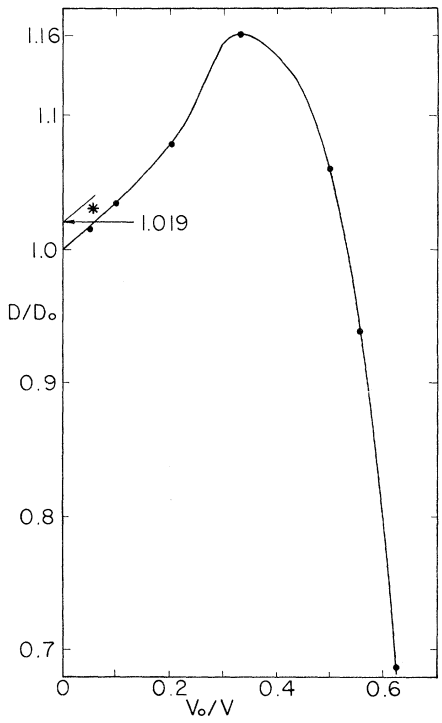

FIG. 2. The ratio of the computed diffusion coefficient to the one calculated from an exponential velocity autocorrelation function according to the Enskog theory versus the volume relative to the close-packed volume. The dots represent the 108-particle results, and the star at $V/V_0 = 20$, a 500-particle result. The heavy line corresponds to a $2/N$ extrapolation to the infinite-particle results with a slope parallel to the one for 108 particles. The intercept at infinite dilution of 1.019 corresponds to the Boltzmann result with the Sonine polynomial correction.

ically evaluated in the Boltzmann limit; however, a calculation of the initial second derivative with respect to time leads to a value larger than that predicted by an exponential decay by a factor of $[6\pi + 27\sqrt{3}]/64$ or 2.5%. The physical origin of this positive deviation arises principally from the smaller collision rates and hence longer relaxation times of the slower particles relative to the energetic particles present in the Maxwell-Boltzmann distribution.

The density dependence of the diffusion coefficient over the entire fluid range, as shown in Fig. 2, is represented with a maximum error of about 20% by the Enskog theory.[5] That theory assumes a velocity autocorrelation function of the Boltzmann form but scaled in time by the ratio of the actual collision rate to the low-density one, or, as can be shown rigorously,[6] by the ratio of the value of $PV/NkT-1$ to its low-density value, namely the second virial coefficient. The latter ratio can easily be expanded in powers of the density and its coefficients represent the major contribution to the density expansion of the diffusion coefficient. This is illustrated by the initial density-dependent term for the ratio of the actual diffusion coefficient to its Boltzmann value (corrected by the Sonine polynomials) which, according to the Enskog theory, is $-1.85V_0/V$, while the computer data yield a value of $-1.5V_0/V$. The small difference represents the effect of correlated three-particle events. Under these circumstances the accuracy of the data does not permit detection of the logarithmic term, which, according to theory, is next in importance beyond the one given above. Perhaps in the two-dimensional systems to be investigated next, this logarithmic term will be detectable, because it is the leading term in the density expansion.

The positively correlated events make their maximum contribution to the diffusion coefficient as a density of about $V/V_0 = 3$ (see Figs.

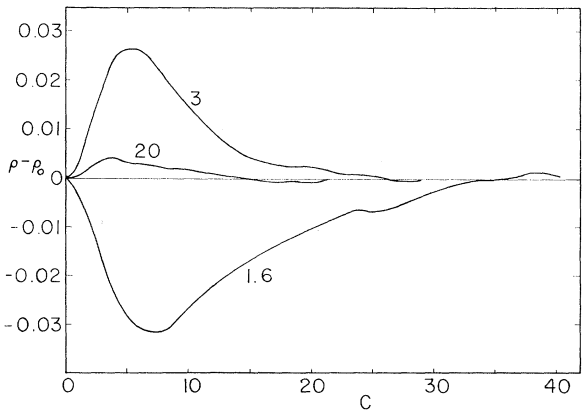

FIG. 3. The difference between the computed velocity autocorrelation function and an exponential one according to the Enskog theory versus the number of mean collision times for 108 particles at V/V_0 of 20, 3, and 1.6.

2 and 3). They lead to the positive structure in the velocity autocorrelation function which extends to about 20 collision times. An effort to find an explanation of this long memory effect (long compared to the relaxation time of 1.5 collision times) is underway. An attempt was made to associate the positive correlation with an initially energetic particle which creates a hot and low-density region which persists for a long time. More details must be worked out in order to verify this mechanism.

At still higher densities the particles surrounding any one particle are more densely packed. The major effect of these neighbors is therefore to reflect the particles, leading to the negative structure in the autocorrelation function discovered earlier[7] and discussed recently in terms of backscattering[8] (see Fig. 3). This negative correlation increases with increasing density and ultimately results in the vanishing of the diffusion coefficient in the crystalline phase.

*Work performed under the auspices of the U. S. Atomic Energy Commission.

[1]E. G. D. Cohen, J. R. Dorfman, M. H. Ernst, L. S. Garcia-Colin, and J. V. Sengers, in Lectures in Theoretical Physics, 1966 (to be published).

[2]B. J. Alder and T. E. Wainwright, J. Chem. Phys. 31, 459 (1959).

[3]S. Chapman and T. G. Cowling, The Mathematical Theory of Nonuniform Gases (University Press, Cambridge, England, 1939).

[4]C. Longuet-Higgins and J. A. Pople, J. Chem. Phys. 25, 884 (1956).

[5]J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, in Molecular Theory of Gases and Liquids (John Wiley & Sons, Inc., New York, 1954).

[6]B. J. Alder and T. E. Wainwright, in The Many-Body Problem, edited by J. Percus (Interscience Publishers, Inc., New York, 1963).

[7]B. J. Alder and T. E. Wainwright, in Transport Processes in Statistical Mechanics, edited by I. Prigogine (Interscience Publishers, Inc., New York, 1958).

[8]J. H. Dymond and B. J. Alder, J. Chem. Phys. 45, 2061 (1966).

INFLUENCE OF ELECTRON CORRELATIONS ON A PLASMA-BROADENED LYMAN-ALPHA LINE*

Earl W. Smith
Department of Physics and Astronomy, University of Florida, Gainesville, Florida
(Received 8 May 1967)

In a previous paper,[1] the relaxation techniques developed by Zwanzig[2] and Fano[3] were used to study the broadening of spectral lines originating from neutral atoms in a plasma. In the relaxation theory, the plasma is represented by three weakly coupled subsystems: an excited atom, a gas of N ions, and a gas of N electrons. In Ref. 1 a calculation of the Lyman-alpha line was made, treating the electron subsystem as an ideal gas of electrons. The purpose of this paper is to present the results of the correction of this ideal-gas approximation.

As in most line-broadening theories, the ions are regarded as infinitely massive classical particles over the time of interest (static-ion approximation). The weak coupling interaction between the atom and its thermal bath of ions and electrons is taken to be a dipole-field interaction which has the form $e\vec{R}\cdot(\vec{\mathcal{E}}_e + \vec{\mathcal{E}}_i)$, where $\vec{R}$ is the position of the atomic electron while $\vec{\mathcal{E}}_e$ and $\vec{\mathcal{E}}_i$ represent the electric fields produced by the electrons and ions, respectively. It is further assumed that the three subsystems are statistically independent and the plasma density matrix is given by a product of density matrices for the atom, the electrons, and the